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# (54) Semicrystalline polymer blend compositions with enhanced interspherulitic and interlamellar strength.

(57) This invention relates to a semicrystalline polymer composition with reinforced spherulite boundaries and interlamellar strength, comprising a major amount of a first semicrystalline polymer and a minor amount of a second semicrystalline homopolymer or a semicrystalline copolymer and a process of making the same.





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This invention relates to polymer compositions having reinforced spherulitic boundaries and improved interlamellar strength.

Polypropylene crystallizes in a spherulitic morphology with inherently weak spherulite boundaries subject to fracture upon impact. The spherulite boundaries, which are critical to strength, tend to be weak causing premature failure under most loading conditions.

Polypropylene blends using ethylene as a toughening agent have been described, see for example "Morphology and Properties of Blends of Polypropylene with Ethylene-Propylene Rubber," Jang et al., Polymer Engineering and Science, V. 24, No.8, Mid-June 1984 describing rubbers dispersed as small particles in the polypropylene matrix, "Polyesters to Polypeptide Synthesis," Encyclopedia of Polymer Science and Engineering, V. 12 pp 443-444 stating that polypropylene blends exhibit improved toughness, "Rubber-Toughening in Polypropylene," Jang et al., Journal of Applied Polymer Science, V. 30, (1985), pp 2485-2504 observing that the rubber particles were randomly dispersed in the polypropylene matrix, were engulfed by the growing matrix, and did not reside preferentially at the spherulite boundaries, "Crystalline Morphology of Polypropylene and Rubber-Modified Polypropylene," Journal of Applied Polymer Science, V. 29, pp 4377-4393 (1984) showing that the rubber phase is not preferentially pushed to the spherulite boundaries and the distribution of the rubber particles is random in the polypropylene matrix. "Propylene/ethylene-co-propylene blends: influence of molecular structure of EPR and composition on phase structure of isothermally crystallized samples," D'Orazio et al., Journal of Materials Science V 26, pp 4033-4047 (1991) discusses amorphous EPR minor component segregation mainly in spherical shaped domains distributed in intra and interspherulitic regions. However, no interspherulitic boundary strengthening was observed. Indeed, because the copolymers discussed are amorphous, they are unable to crystallize and hence cannot provide reinforced spherulite boundaries and interlamellar links, as in the present invention.

Several U.S. patents are also directed to propylene ethylene polymer compositions see for example 4946898 and 4948841 to Kasahara et al., 4774292 to Thiersault et al., and 4395519 to Minami et al. The above patents do not disclose a semi-crystalline polymer blend where the copolymer of the blend is preferentially located at the spherulite boundaries as does the present invention.

This invention provides a semicrystalline polymer composition with reinforced spherulite boundaries and interlamellar links, comprising a major amount of a first semicrystalline polymer and a minor amount of a second semicrystalline homopolymer or a semicrystalline copolymer and a process of making the same. The second semicrystalline homopolymer or copolymer will be preferentially located at the spherulite boundaries. As used herein, a minor amount means about .1 to about 50 wt.% and a major amount means at least about 50 wt.% up to about 99.9 wt.%.

By this invention a first semicrystalline homopolymer is blended with a second semicrystalline homopolymer or semicrystalline copolymer, based on the same semicrystalline polymer as the first semicrystalline homopolymer. Both the second semicrystalline homopolymer and the semicrystalline copolymer have a lower degree of crystallinity and crystallization temperature than the first semicrystalline homopolymer. The first semicrystalline homopolymer and second semicrystalline homopolymer or copolymer are mixed through melt or solution blending, and then processed under cooling conditions which allow the first semicrystalline homopolymer to crystallize before the second semicrystalline homopolymer or copolymer located at the spherulite boundaries. As the first semicrystalline homopolymer crystallizes, the noncrystallizable segments of the semicrystalline copolymer or second homopolymer are rejected from the lamellae within and between spherulites. Probably, the crystallization of the crystallizable segments in adjacent lamellae and/or spherulites allows for strengthening of the interlamellar and interspherulitic regions by adding to tie molecule concentration. These regions would otherwise have a tendency to be weak under many loading conditions.

The semicrystalline copolymer or second homopolymer polymer chains are comprised of crystallizable and noncrystallizable segments. As used herein noncrystallizable segments means that such segments will not crystallize under the same conditions that the first homopolymer crystallizes under. Crystallizable segments means that such segments will crystallize under the same conditions as the first homopolymer.

All polymers referred to herein are semicrystalline polymers. Semicrystalline polymers have both a crystalline phase and an amorphous phase, the former residing in a plate-like lamellar structure. During solidification, the lamellae become radially oriented into structures known as spherulites. During crystallization, the lamellae and spherulites have a tendency to reject low molecular weight polymer as well as various impurities into interlamellar and interspherulitic regions. This segregation often results in poor mechanical performance since the interlamellar and interspherulitic regions are local areas of mechanical weakness.

By this invention a first homopolymer is blended with a copolymer or a second homopolymer. Such copolymer or second homopolymer must be miscible in the melt with the first homopolymer at the concentrations used. The copolymer is comprised of the first homopolymer and a comonomer. The copolymer is

about .1 to about 50 wt.%, preferably 5 to 30 wt.%, more preferably about 10 wt.%, of the polymer blend formed by this invention. When a second homopolymer is mixed with the first homopolymer, the second homopolymer is also about .1 to about 50 wt.% of the polymer formed, preferably 5 to 30 wt.%, more preferably about 10 wt.%.

The amount of comonomer in the copolymer can range from about .1 to about 70 wt.% depending on the comonomer used. The amount of comonomer must be such that the copolymer is miscible in the melt with the homopolymer and the copolymer must be capable of cocrystallizing in the blend during crystallization. For example, when ethylene is the comonomer, it may be present in an amount up to 8 wt.%. Ethylene amounts greater than 8 wt.% would not provide the necessary melt miscibility. Such melt miscibilities are easily determinable by those skilled in the art (see for example Lohse, "The Melt Compatibility of Blends of Polypropylene and Ethylene-Propylene Copolymers," Polymer Engineering and Science, November 1986, Vol. 26, No. 21, pp 1500-1509). As used herein comonomer means one of the monomers comprising the copolymer.

The copolymers used in the present invention may be olefin based copolymers, meaning that the polymer chain backbone is an olefin. The copolymers may further be random copolymers or block copolymers. A block copolymer is one in which the monomer units occur in relatively long alternate sequences on a chain.

The first homopolymer may be a polyolefin. The first homopolymer may be selected from, for example, polypropylene, and polyethylene. Preferably, the first homopolymer is polypropylene, more preferably isotactic polypropylene. The comonomers of the copolymer are selected from ethylene, and alpha olefins when the first homopolymer is polypropylene, with ethylene being preferred. Hence, the copolymers utilized with polypropylene as the first homopolymer are propylene ethylene and propylene alpha olefins, with propylene ethylene being preferred. When polyethylene is the first homopolymer the comonomers may be selected e.g. from alpha olefins, vinyl acetate, and methyl acrylate, with alpha olefins being preferred. Hence, the copolymers utilized when polyethylene is the first homopolymer are e.g. ethylene alpha olefins, ethylene vinyl acetate, and ethylene methyl acrylate. The alpha olefins may be selected from butene, hexene, octene, and 4-methylpentene. A principal condition is that the copolymers be melt miscible with the homopolymer.

Alternatively, the first homopolymer may be blended with a second homopolymer. In this case the first homopolymer will be a homopolymer displaying either isotactic or syndiotactic tacticity. The second homopolymer will be the same homopolymer as the first homopolymer, however its backbone chain will have the same tacticity as the first homopolymer in addition to nonstereoregular sequences, sequences of a different stereoregularity, or a combination of nonstereoregular sequences and sequences of a different stereoregularity, or isolated nonstereoregular sequences. Such additional sequences of the second homopolymer probably lower the crystallinity and the crystallization temperature of the second homopolymer, allowing the first homopolymer to form spherulites before the second homopolymer located at the spherulite boundaries crystallizes.

The nonstereoregular sequences, sequences of a different stereoregularity, or a combination of nonstereoregular sequences and sequences of a different stereoregularity of the second homopolymer will be in diblock, triblock, or multiblock form. Alternatively, the second homopolymer can contain isolated nonstereoregular units in a random form.

As used herein, the nonstereoregular sequences or units are atactic sequences or units and the sequences of a different stereoregularity are syndiotactic sequences when the first homopolymer is isotactic homopolymer, and are isotactic sequences when the first homopolymer is syndiotactic homopolymer. In general all that is needed is that a portion of the second homopolymer backbone chain be identical to that of the first homopolymer, and that the remainder of the second homopolymer comprise homopolymer in nonstereoregular sequences, sequences of a different stereoregularity, a combination of the two, or isolated nonstereoregular units.

For example, if the first homopolymer was isotactic polypropylene, the second homopolymer could consist of isotactic and atactic polypropylene, or isotactic and syndiotactic polypropylene in diblock, triblock, or multiblock form. Alternatively the second homopolymer could consist of blocks of isotactic, syndiotactic and atactic polypropylene in a similar arrangement. Lastly, the second homopolymer could consist of isotactic polypropylene with isolated atactic units in random form. Polystyrenes may also be used as the first and second homopolymers as described above.

The amount of the second homopolymer backbone chain which must be identical to that of the first homopolymer (displaying the same tacticity) is an effective amount which will enable the second homopolymer to cocrystallize and thereby attach itself to the ends of the lamellae across adjacent spherulite boundaries of the spherulites formed by the first homopolymer. The amount of second homopolymer which must differ from that of the first homopolymer is an effective amount which will allow the first homopolymer to crystallize into spherulites first, allowing the second homopolymer residing at the spherulite boundaries to cocrystallize across lamellae of adjacent spherulites once the spherulites of the first homopolyer have formed. The amount of second homopolymer

backbone chain which must be identical to that of the first homopolymer is at least about 5%. The amount of the second homopolymer backbone chain which must differ from that of the first homopolymer is at least about 0.5%. A portion of the second homopolymer may remain between the spherulite lamallae of the first homopolymer, cocrystallize and attach itself within adjacent lamellae within the spherulite of the first homopolymer thereby increasing tie molecule concentration and further increasing the polymer's toughness. As used herein by differing from that of the first homopolymer is meant the nonstereoregular sequences, and/or stereoregular sequences of a different stereoregularity, or isolated nonstereoregular units in a random fashion.

Such second homopolymers can be easily prepared by one skilled in the art (See for example, J. Am. Chem. Soc, 1990, 112, 2030-2031, "rac-[Ethylidene(1-$\eta^5$-tetramethylcyclopentadienyl) (1-$\eta^5$-indenyl)] dichlorotitanium and its Homopolymerization of Propylene to Crystalline-Amorphous Block Thermoplastic Elastomers, Mallin, Rausch, Lin, Dong, and Chien; Macromolecules, Vol. 25, No. 4, 1992, 1242-1252, "Crystalline-Amorphous Block Polypropylene and Nonsymmetric ansa-Metallocene Catalyzed Polymerization," Llinas, Dong, Mallin, Rausch, Lin, Winter, and Chien; Macromolecules, 1990, 23, 3559-3568, "Degree of Stereochemical Control of rac-Et[Ind]$_2$ZrCl$_2$/MAO Catalyst and Properties of Anisotactic Polypropylenes[1]," Rieger, Mu, Mallin, Rausch, and Chien.

When the first homopolymer is polypropylene the second homopolymer will be polypropylene having isolated methyl groups in a nonstereoregular sequence. Likely, the nonstereoregular sequence of the second homopolymer or the comonomer of the copolymer disrupts crystallinity and hence lowers the crystallization temperature of the homopolymer and copolymer respectively.

After the first homopolymer has been blended with either the copolymer or a second homopolymer, the blend is melted and then allowed to cool at a rate dictated by the crystallization temperature and crystallization kinetics of the specific blend. This is easily determined by one skilled in the art. The first homopolymer must have completely formed spherulites before the copolymer or second homopolymer at the spherulite boundaries begins to crystallize. This means that primary crystallization must have been completed in the first homopolymer prior to onset of crystallization of the second homopolymer or copolymer at the spherulite boundaries. Primary crystallization occurs during spherulite formation of the first semicrystalline homopolymer. The desired cooling rate will be a function of the difference in crystallization temperature and crystallization rates between the first homopolymer and copolymer or the first homopolymer and the second homopolymer. The greater the difference the faster the cooling rate can be. The difference in crystallization temperature of the first homopholymer and copolymer or second homopolymer is about 20 to about 100°C, preferably about 50 to about 100°C with the crystallization temperature of the copolymer or second homopolymer being lower.

During spherulite formation, likely the first homopolymer will crystallize first, but allow the crystallizable segments of the second homopolymer or copolymer to cocrystallize with it. However, the noncrystallizable segments of the copolymer or second homopolymer will be rejected from between adjacent lamellae within or between spherulites. The crystallizable segments of the copolymer or homopolymer chains which are in the body of the spherulites attach themselves to adjacent lamellae, enhancing the link between these lamellae by adding to interlamellar tie molecule concentration. The crystallizable segments of the copolymer or homopolymer chain which are at the spherulite boundaries attach themselves to the lamellae across adjacent boundaries enhancing the concentration of interspherulitic tie molecules. In this way, the molecular link between spherulites and lamellae becomes enhanced, resulting in improved failure resistance and mechanical performance.

The following example is illustrative and not limiting in any way.

EXAMPLE 1

900 grams of 35 melt flow rate polypropylene homopolymer was combined with 100 grams of 30.1 melt flow rate ethylene propylene random copolymer containing 5.1 percent ethylene units. The two polymers were then dry-blended by mixing in a plastic bag. The mixture was then extruded at a temperature of 180°C and pelletized.

10 pellets were then placed between two aluminum sheets which were then placed in a compression mold and melted at 200°C for one minute. 24000 pounds of pressure were applied to a 12" by 12" mold containing the melt. The material was then cooled at a rate of 5°C per minute and held at 130°C for 30 minutes under pressure. The material was then removed from the mold and the aluminum sheets peeled off.

EXAMPLE 2

6.3 grams of 200 melt flow rate polypropylene homopolymer was combined with 0.7 grams of a crystalline-amorphous block polypropylene prepared in accordance with J. Am. Chem. Soc. 1990, 112, 2030-2031, "rac-[Ethylidene(1-$\eta^5$-tetramethylcyclopentadienyl) (1-$\eta^5$-indenyl)]dichlorotitanium and its Homopolymerization of Propylene to Crystalline-Amorphous Block Thermoplastic Elastomers, Mallin, Rausch, Lin, Dong, and Chien, only polymerized at 30°C. The two polymers were dry blended by mixing

in a paper cup. The mixture was then extruded at a temperature of 190°C and pelletized.

5 grams were then placed within a tensile mold 0.020 inches thick, 0.1 inches wide, and 1 inch long between two aluminum sheets in a compression mold and melted at 200°C for 2 minutes under slight pressure. 5,000 lbs of pressure were applied to the 12" x 12" platens containing the melt. The material was then cooled at a rate of approximately 100°C per minute by transferring the mold and aluminum between water cooled platens. An impact specimen was prepared by taking some of the tensile specimens and remolding them into an IZOD type impact specimen using the same molding conditions as above. Tensile properties of this blend show an elongation of 300%, versus 5.7% for the 200 melt flow rate base polypropylene alone. Impact energy was 0.4 foot-pounds for the blend versus 0.04 foot-pounds for the base polypropylene.

## Claims

1. A polymer composition comprising a major amount of a first semicrystalline homopolymer and a minor amount of a second semicrystalline homopolymer or semicrystalline copolymer, wherein said second semicrystalline homopolymer or semicrystalline copolymer is preferentially located at the spherulite boundaries and between the lamellae of said first semicrystalline homopolymer.

2. A composition according to claim 1 wherein said first semicrystalline homopolymer is selected from polypropylene and polyethylene.

3. A composition according to claim 1 wherein said first semicrystalline homopolymer is polypropylene and said semicrystalline copolymer is propylene ethylene.

4. A composition according to claim 1 wherein said first semicrystalline homopolymer is a homopolymer having tacticity and said second homopolymer is the same homopolymer as said first homopolymer wherein said second homopolymer has an effective amount of the same tacticity as said first homopolymer in addition to an effective amount of sequences selected from nonstereoregular sequences, sequences of a different stereoregularity, nonstereoregular sequences and sequences of a different stereoregularity in diblock, triblock, or multiblock form, and isolated nonstereoregular units in random form.

5. A composition according to claim 4 wherein when said first homopolymer is an isotactic homopolymer, said nonstereoregular units and sequences are atactic units and sequences and said different stereoregular sequences are syndiotactic sequences, and wherein when said first homopolymer is a syndiotactic homopolymer, said nonstereoregular units or sequences are atactic units or sequences and said different stereoregular sequences are isotactic sequences.

6. A composition according to claim 5 wherein said first semicrystalline homopolymer is selected from polypropylene and polystyrene.

7. A composition according to claim 4 wherein said first semicrystalline homopolymer is isotactic polypropylene and said second semicrystalline homopolymer is isotactic polypropylene in multiblock form with atactic polypropylene.

8. A composition according to any of claims 4 to 7 wherein an effective amount of the same tacticity as said first homopolymer is at least about 5%.

9. A composition according to any of claims 4 to 8 wherein an effective amount of sequences selected from the group consisting of nonstereoregular sequences, sequences of a different stereoregularity, nonstereoregular sequences and sequences of a different stereo regularity in diblock, triblock, or multiblock form, and isolated nonstereoregular units in random form is at least about 0.5%.

10. A process of forming a polymer composition having increased spherulite boundary and interlamellar strength comprising the steps of:
    (a) mixing a first semicrystalline homopolymer with a semicrystalline copolymer or a second semicrystalline homopolymer wherein said semicrystalline copolymer or said second semicrystalline homopolymer has a lower crystallization temperature than said first semicrystalline homopolymer to form a polymer mixture;
    (b) melting said polymer mixture wherein said semicrystalline copolymer and said first semicrystalline homopolymer or said second semicrystalline homopolymer and said first semicrystalline homopolymer are melt miscible;
    (c) crystallizing said melted polymer mixture by cooling at a rate sufficient to allow said first semicrystalline homopolymer to form spherulites and thereafter continuing to cool to allow said semicrystalline copolymer or said second semicrystalline homopolymer to crystallize at the spherulite boundaries.

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number
EP 92 31 1504

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
|---|---|---|---|
| X | EP-A-0 423 962 (NIPPON PETROCHEMICALS)<br>* page 2, line 16 - page 3, line 32; claims 1,2 * | 1,2,10 | C08L23/12<br>C08L23/06 |
| X | FR-A-2 009 263 (FARBWERKE HOECHST)<br>* page 3, line 29 - line 39; claims 1-4 * | 1-3,6,8,10 | |
| X | US-A-3 888 949 (C. SHIH)<br>* column 3, line 42 - column 4, line 2; claims 1-5 * | 1,2,10 | |
| X | DE-A-1 420 559 (MONTECATINI SOCIETA GENERALE PER L'INDUSTRIA MINERARIA E CHIMICA)<br>* page 5, line 26 - page 6, line 19; claim 2 *<br>* page 7, line 26 - page 8, line 2 *<br>* page 10, line 2 - line 15 * | 1,2,4-10 | |
| A | GB-A-2 241 244 (THE ACADEMY OF APPLIED SCIENCE)<br>* claims 1-8 * | 4,5,9 | TECHNICAL FIELDS SEARCHED (Int. Cl.5)<br>C08L |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 14 APRIL 1993 | R. E. Goovaerts |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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